

SPECIFICATION

METHOD FOR TREATING ORGANIC COMPOUND-CONTAINING
WASTE WATER AND SYSTEM CONDUCTING SAME

BACKGROUND OF THE INVENTIONS

Field of the Inventions

This inventions relates to a method for treating organic compounds contained in waste water by electrolytic decomposition and, in particular, relates to a method of practical scale for treating organic compounds by electrolytic decomposition to form inorganic compounds such as carbon dioxide, water, etc. without forming harmful and bad-smelling byproducts. Further, this invention relates to a method for treating organic compounds contained in waste water together with organic suspended solids (SS) by oxidative decomposition to decrease the total organic carbon (TOC) concentration and the chemical oxygen demand (COD) in the waste water without removing the organic suspended solids as organic compounds in advance from waste water containing them, and a system conducting same. Furthermore, this invention relates to a method of practical scale for treating organic nitrogen compound-containing waste water by decomposing organic compounds contained therein into harmless inorganic compounds such as nitrogen gas, carbon dioxide gas, water, etc.

Prior Art

Various kinds of waste water from plants, stockfarm, domestic origins and others contain such as dimethyl sulfoxide, aliphatic alcohol and aromatic alcohol as well as organic nitrogen compounds, organic suspended solids, etc., which might pollute environments.

With regard to industrial waste water among others, exhaustion of such organic compounds should be decreased to a level of tolerance limit. Especially, organic nitrogen compounds cause eutrophication when they are released in water, while they themselves behave as harmful substances in the air and further take part in photochemical reaction to cause a phenomenon of secondary combined pollution. These organic nitrogen compounds arise, for example, from protein used as a starting material of feed production for domestic animal, poultry, fish, etc. and in food production, and are also derived from product leakage during production processes of chemicals and pharmaceuticals, or from byproducts or starting materials thereof.

When waste water to be treated contains organic suspended solids, it is hard to directly supply such waste water to a biological or physicochemical treatment system. Accordingly, the waste water which contains organic suspended solids should be subjected to a pretreatment such as filtration and coagulation-sedimentation to remove the suspended solids followed by biological or physiochemical treatment thereof. It is costly to install large equipment such as filtering tanks and coagulation-sedimentation tanks. Further, the thus removed organic suspended solids should be treated as an industrial waste, which additionally increases the cost.

There have been employed many treating methods to reduce these organic compounds in waste water, such as a biodegradation treatment including an activated sludge process, an ozone oxidation treatment and an electrochemical treatment. The electrochemical treatment has advantages of being easier operation and, in addition, more compact construction and shorter time of treatment compared with biodegradation and ozone oxidation.

From the above mentioned viewpoints, there has been developed a treatment by electrolytic decomposition in which various kinds of anodic materials such as platinum, lead oxide and tin oxide are used.

Industrial waste water from plants often contains strongly corrosive compounds, which easily corrode the anodic materials as described above.

Although stable electrolytic decomposition can be done by means of a platinum electrode at current density of about 0.1 A/cm² during the decomposition treatment, the electrode degrades markedly and shortens its durability when the current density is increased to 0.2 A/cm² or more to improve the effect of treatment.

Diamond is expected as a useful electrode material for waste water treatment by electrolytic decomposition because of its high chemical stability and electric conductivity caused by boron or nitrogen doping.

Fujishima, et al. reported that a boron-doped diamond electrode has a quite wide potential window and behaves stably even in an aqueous solution of high corrosive properties (see, *Electrochemistry*, vol. 67(1999), 389).

Further, Fujishima et al. also reported that NO_x is effectively reduced to ammonium by the diamond electrode (see, *Journal of Electroanalytical Chemistry*, vol. 396 (1995), 233).

Japanese Patent No. 7-299,467 discloses that organic compounds can be oxidatively decomposed by means of a boron-doped diamond electrode, while Japanese Patent No. 7-241,549 discloses that organic suspended solids can be removed by filtration when such solids-containing water is treated.

However, there has not been sufficiently reported a practical technique for treating waste water from plants, etc. by means of the above mentioned diamond electrode under a condition of high current density. On the other hand, a considerable amount of oxygen and hydrogen is generated by electrolytic decomposition at high liquid flow linear velocity, and retained in an electrolytic reaction tank as gas contents, which interferes contact between waste water and a diamond electrode so that the current efficiency is reduced while the current density is locally increased to an extent. As a result, a diamond thin layer formed on a substrate as an electrode is peeled off from the substrate, which causes a problem.

In the case of waste water treatment by electrolytic decomposition using a metal electrode such as platinum, organic suspended solids are deposited on the metal electrode if the waste water contains them and is directly treated by electrolytic decomposition. This causes an increase in the voltage between electrodes and a great decrease in the energy efficiency, thereby lowering an effect to remove soluble organic substances. Further, activity of electrodes might be rapidly decreased by repeated electrode changes to sharply shorten their durability. Therefore, according to conventional electrolytic treatments of waste water which contains organic suspended solids, they should be removed by pre-treatments such as filtration and coagulation-sedimentation followed by an electrolytic treatment of the waste water.

Further, a treating system and method described in Japanese Patent No. 7-299,467 is applied to various kinds of different solutions used for, for example, treating waste water of halogenated silver photography, but there is no description with regard to organic suspended solids. More precisely, the above mentioned invention discloses that an electrolytic treatment using diamond electrodes can be applied to arbitrary solutions which contain solutes easily oxidized by electrolytic decomposition. It has thus been common knowledge in conventional electrolytic oxidation treatments that suspended solids are removed in advance followed by a treatment of solutes. As a matter of course, there is no disclosure nor suggestion in Japanese Patent No. 7-299,467 about direct application of an electrolytic treatment using diamond electrodes to waste water which contains organic suspended solids without pre-treating such solid in the water by a pre-treatment. According to Japanese Patent No. 7-299,467, however, it is an unexpected way of thinking and is quite uneasy to those who skilled in the art to directly apply a treatment by electrolytic decomposition using diamond electrodes to organic suspended solids-containing waste water. That is to say, it has been conventionally unusual to apply such the direct application of the treatment by electrolytic decomposition using diamond electrodes to

waste water which contains organic suspended solids without removing them from the waste water by a pre-treatment.

In a treatment by electrolytic decomposition using diamond electrodes as a cathode and an anode, organic nitrogen compounds are oxidized to NO_x or a nitrate ion on the anode and reduced to ammonia on the cathode. Thus reduced ammonia is then oxidized to a nitrate ion on the anode and finally exhausted as a nitrogen gas. As the treatment effectiveness is low because of repeated oxidation and reduction on both anode and cathode as described above, it has been necessary in any case to develop a practical technique for treating waste water which contains organic nitrogen compounds.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the invention to provide a method of practical scale for treating organic compounds-containing waste water from plants, etc. by electrolytic decomposition using diamond electrodes to generate harmless inorganic compounds without forming harmful and bad-smelling byproducts. Further object of this invention is to provide a method and system for treating waste water which contains soluble organic substances and organic suspended solids contained therein are decomposed and removed at the same time to reduce the total organic carbon (TOC) concentration and the chemical oxygen demand (COD) by oxidatively decomposing the soluble organic substances together with the organic suspended solids in the waste water without inevitably removing such solids in advance. Another object of this invention is to provide a method for treating waste water in which organic nitrogen compounds in waste water from plants, etc. are treated by electrolytic decomposition using diamond electrodes to remove as harmless inorganic compounds such as carbon dioxide, nitrogen gas and water at high efficiency.

DETAILED DESCRIPTION

In the first method for treating organic compounds containing waste water claimed in claim 1 of this invention, there is provided a method for electrochemically detoxifying organic compounds contained in waste water using diamond electrodes at least as an anode, in which current density is 0.5 to 10 A/cm^2 and liquid flow linear velocity is 200 to 10,000 m/hr .

In the second method for treating organic compounds containing waste water claimed in claim 2 of this invention, there is provided a method for electrochemically detoxifying organic compounds contained in waste water, in which diamond electrodes

are used at least as an anode, while pH of the waste water is adjusted to be alkaline.

In the third method for treating organic compound containing waste water claimed in claim 3 of this invention, there is provided a method for electrochemically detoxifying organic suspended solids contained in waste water as organic compounds, in which diamond electrodes are used at least as an anode to treat the organic suspended solids by electrolytic decomposition.

In a treating method claimed in claim 4 of this invention, there is provided a method claimed in claim 1, 2 or 3 in which diamond electrodes are used as both of an anode and a cathode to undergo change of electrodes.

In the fourth method for treating organic compounds containing waste water claimed in claim 5 of this invention, there is provided a method for electrochemically detoxifying organic nitrogen compounds contained in waste water as organic compounds, in which a first step treatment by electrolytic decomposition is conducted using diamond electrodes as an anode and a cathode, and then a second step treatment by electrolytic decomposition is conducted using the diamond electrodes as a cathode and metal electrodes as an anode.

In a treating method claimed in claim 6 of this invention, there is provided a method claimed in claim 5 in which sulfate ions are added to organic compounds-containing waste water when a first step treatment by electrolytic composition is conducted.

In a treating method claimed in claim 7 of this invention, there is provided a method claimed in claim 5 or 6 in which chloride ions are added to waste water after a first step treatment thereof by electrolytic decomposition when a second step treatment by electrolytic composition is conducted.

In a treating method claimed in claim 8 of this invention, there is provided a method claimed in any one of claims 2 to 7 for treating waste water by electrolytic decomposition using diamond electrodes, in which current density on the surface of diamond electrodes is 0.001 to 10 A/cm² and liquid flow linear velocity is 10 to 10,000 m/hr during the treatment by electrolytic decomposition. method claimed in any one of claims 2 to 7 for treating waste water by electrolytic decomposition using diamond electrodes, in which current density on the surface of diamond electrodes is 0.001 to 10 A/cm² and liquid flow linear velocity is 10 to 10,000 m/hr during the treatment by electrolytic decomposition.

In a treating method claimed in claim 9 of this invention, there is provided a method claimed in any one of claims 2 to 8 for treating waste water by electrolytic decomposition using diamond electrodes, in which current density on the surface of

diamond electrodes is 0.5 to 10 A/cm² and liquid flow linear velocity is 200 to 10,000 m/hr during the treatment by electrolytic decomposition.

In a treating method claimed in claim 10 of this invention, there is provided a method for controlling liquid flow linear velocity of the treatment by electrolytic decomposition in a method claimed any one of said claims 1 to 9 so as to satisfy the following formula 1:

$$\text{Formula 1: liquid flow linear velocity (m/hr)} \geq 400 \times (\text{current density (A/cm}^2\text{)} - 0.5) + 200$$

In a treating method claimed in claim 11 of this invention, there is provided a method for controlling liquid flow linear velocity of said treatment by electrolytic decomposition in a method claimed any one of said claims 1 to 10 so as to satisfy the following formula 2:

$$\text{Formula 2: liquid flow linear velocity (m/hr)} \geq 1,000 \times (\text{current density (A/cm}^2\text{)} - 0.5) + 200$$

And a system for treating organic compounds-containing waste water claimed in claim 12 of this invention comprises diamond electrodes to conduct a treatment by electrolytic decomposition of organic suspended solids contained in waste water as organic compounds.

A system for treating organic compounds-containing waste water claimed in claim 13 of this invention, there is provided a system for treating organic compounds-containing waste water claimed in claim 12 in which a treatment by electrolytic decomposition using diamond electrodes is conducted at current density of 0.001 to 10 A/cm² and liquid flow linear velocity of 10 to 10,000 m/hr.

In a system for treating organic compounds-containing waste water claimed in claim 14, there is provided a system for treating organic compounds-containing waste water claimed in claim 12 or 13 in which change of electrodes are conducted using diamond electrodes for both of a cathode and an anode.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a relationship between linear velocity to supply waste water to an electrolytic reaction tank and current density of diamond electrodes in the electrolytic reaction tank according to the first treating method of this invention.

Fig. 2 is a block diagram of a system for conducting the first treating method of this invention.

Fig. 3 is another block diagram of a system for conducting the first treating method of this invention.

Fig. 4 is yet another block diagram of a system for conducting the first treating method of this invention.

Fig. 5 is a block diagram of a system for conducting the fourth treating method of this invention.

Fig. 6 is another block diagram of a system for conducting the fourth treating method of this invention.

Fig. 7 is yet another block diagram of a system for conducting the fourth treating method of this invention.

In Figs. 1 to 4, numerals 1, 2, 3 and 11 designate an electrolytic reaction tank, numerals 4, 5 and 6 designate a waste water storage tank, a treated water storage tank and a water receiving tank, and numerals 6' and 11' designate a vent zone. In Figs. 5 to 7, numerals 1, 11, 12 and 13 designate an electrolytic reaction tank for the first step electrolytic decomposition, and numerals 2, 21, 22 and 23 designate that of for the second step electrolytic decomposition, while numerals 3, 4 and 5 designate a storage tank, a storage tank for waste water to be treated and a treated water storage tank, respectively.

THE PREFERRED EMBODIMENTS

There will be described in detail the first to fourth methods for treating organic compounds-containing waste water of this invention as in the following.

First method for treating organic compounds-containing waste water

First of all, the first method for treating organic compounds-containing waste water of this invention will be described.

Organic compounds to be treated by the first treating method of this invention are not limited to specific ones but may include any of those compounds which can be decomposed by an electrochemical treatment to inorganic compounds such as carbon dioxide and water.

Further, as there is no restriction with regard to concentration of these organic compounds, they may be used in any concentration and, in some cases, may be concentrated before the first treating method. However, preferable concentration of the organic compounds is 0.5 to 20 g/liter from a standpoint of electrolytic efficiency of diamond electrodes ("liter" and "milliliter" will hereinafter be referred to as "L" and "mL", respectively).

Current density used in the first treating method of this invention is 0.5 to 10 A/cm². At current density less than 0.5 A/cm², a surface area of electrode should be large to a certain extent and an electrolytic reaction tank of large scale is required in

order to treat a large amount of waste water from plants, etc. by electrolytic decomposition using diamond electrodes of high current efficiency on a practical scale to decrease the organic compounds contained therein to a predetermined level. This causes a huge increase in both system and running costs.

At current density more than 10 A/cm², voltage between electrodes is increased and consumed as thermal energy, which is quite uneconomical and also undesirable for durability of diamond electrodes.

It is preferable to increase the liquid flow linear velocity with an increase in the current density, and is important to keep it at a level of 200 m/hr or more so that the total organic carbon (TOC) removal rate of 70 % or more in three hours is obtained within a range of the current density as described above and that a gas content formed by an electrolytic reaction is effectively removed with the water flow.

An upper limit of the liquid flow linear velocity is not especially prescribed but is generally about 10,000 m/hr because the excessively high linear velocity results in insufficient contact between organic compounds in the liquid and the diamond electrodes and does not promote electrolytic decomposition of organic compounds effectively.

Further, it is preferable to control the liquid flow linear velocity to satisfy the following formula 1:

$$\text{Formula 1: liquid flow linear velocity (m/hr)} \geq 400 \times (\text{current density (A/cm}^2\text{)} - 0.5) + 200$$

In other words, the liquid flow linear velocity is controlled to be on the lower solid line or in its upper area of the graph drawn in Fig. 1 which shows a relationship between the linear velocity and the current density.

If the liquid flow linear velocity resides in an area below the lower solid line, a large amount of gas formed by electrolytic reaction stays in a reaction tank and affects the current efficiency, while the current density is increased locally to cause a problem, i.e., a thin layer of diamond electrode is peeled off from the substrate.

More preferably, the liquid flow linear velocity is controlled to satisfy the following formula 2:

$$\text{Formula 2: liquid flow linear velocity (m/hr)} \geq 1,000 \times (\text{current density (A/cm}^2\text{)} - 0.5) + 200$$

In other words, the liquid flow linear velocity is controlled to be on or above an upper area of the dotted line, thereby more advantageous effect being obtained.

So long as the above mentioned relationship between the liquid flow linear velocity and the current density is satisfied, organic compounds contained in waste

water can be electrochemically oxidized and decomposed with quite high efficacy according to the first treating method of this invention.

When waste water is treated by electrolytic decomposition using diamond electrodes at least as an anode, a large amount of hydroxyl radical is formed in general, which may promote indirect oxidative decomposition of organic compounds.

Formation of hydroxyl radical is increased by a diamond electrode more predominantly compared with other electrode materials and is especially enhanced under an alkaline condition, rather than neutral, of higher OH^- ion concentration obtained by adjusting pH of waste water.

The thus increased formation of hydroxyl radical raises an effect of oxidative decomposition of organic compounds in waste water, which is further increased synergistically with electrolytic decomposition thereof using diamond electrodes.

Diamond electrodes used for electrochemically treating waste water under the above mentioned condition include those which deposited an electrically conductive thin layer of diamond on the surface of an electrically conductive metal material such as Nb, Ta, Ti, Mo, W and Zr as a substrate, those which synthesized a thin layer of diamond on the surface of wafer as a semi-conductive substrate such as silicon wafer, and electrically conductive polycrystalline diamond deposition-synthesized as a plate-like shape without using a substrate.

Such an electrically conductive thin layer of diamond generally includes doped one prepared by doping a certain amount of boron or nitrogen thereon to endow electrical conductivity.

A suitable amount of doping is in the range of 50 to 10,000 ppm per carbon contained in the thin layer of diamond, an excessively smaller amount thereof exhibiting less technical significance of doping while an excessive amount saturating the doping effect.

In general, a diamond electrode used in this invention is a plate type in shape and may include an interstice plate or other types.

There may also be used a carbon powder or other powdery materials coated with an electrically conductive thin layer of diamond as an electrode. When a diamond electrode of powdery type is used, the electrode may, for example, be dispersed in electrolyte and fluidized to form a fluidized bed which plays a role as an anode.

Further, the above mentioned substrate as an anode may be porous in nature, or a porous synthetic resin material supported with a powder of electrically conductive diamond, which has an increased surface area. The electrode of increased surface area comprises a fixed bed which acts as an anode. The diamond electrode is not

necessarily crystalline but may be amorphous in nature.

In the first treating method of this invention, the diamond electrode may also be used as a cathode, thereby the cathode and anode being periodically changed to conduct a treatment by electrolytic decomposition.

The above mentioned diamond electrode has a quite wider potential window compared with other electrode materials and allows to conduct the decomposition treatment of organic compounds effectively under a condition as described above while controlling hydrogen and oxygen formed by electrolytic decomposition of water.

Liquid temperatures in an electrolytic reaction tank are not especially restricted but preferably 10 to 95°C in the first treating method, because electrolytic decomposition of organic compounds does not proceed successfully when the temperature is excessively low, while formation of gas contents is increased at higher temperatures to inhibit sufficient contact between waste water and the surface of electrode.

According to the first treating method, organic compounds contained in waste water from plants, etc. can be treated by electrolytic decomposition quite effectively in a small-sized system of a decreased contact surface effected by improved current efficiency by the use of diamond electrodes of non-corrosive properties against acid and alkali due to chemical stability thereof under a condition of the satisfactory relationship between the current density and the liquid flow linear velocity as described above.

As a result, it is possible to electrochemically treat waste water from plants, etc. with ease by means of a compact system of practical scale to decompose organic compounds contained therein to harmless inorganic compounds such as carbon dioxide and water without forming harmful and bad-smelling byproducts.

Further, according to the first treating method of this invention, it is also possible to treat organic compounds-containing waste water by electrolytic decomposition using diamond electrodes under the above mentioned condition while separating and removing gas contents formed by electrolytic decomposition of organic compounds.

The gas contents may be separated and removed by any manner including, for example, by means of a general gas-liquid separator itself or an electrolytic reaction tank provided with an upper vapor phase section (space) and a vent (vent tube, vent opening, etc.) on a top portion thereof.

More precisely, as bubbles are easily go up in water and moved into the vapor phase, the gas contents such as carbon dioxide and nitrogen gas formed through the

treatment by electrolytic decomposition result in an upper vapor phase section which is easily separated from a lower liquid phase section, while formation of oxygen or hydrogen is controlled so long as the above mentioned relationship between the current density and the liquid flow linear velocity is satisfied, and even if oxygen or hydrogen is formed, it goes up together with carbon dioxide, etc. into the vapor phase section or it is accompanied by the liquid flow and taken out of the reaction tank without causing residence thereof nor a fall down of the current efficiency, thereby electrolytic reaction being conducted smoothly.

Accordingly, it is possible to easily separate water and the gas contents formed through the treatment by electrolytic decomposition by means of the above mentioned electrolytic reaction tank provided a vent section and a vapor phase section.

According to the first treating method, there may also be used a plurality of electrolytic reaction tanks to treat organic compounds-containing waste water by electrolytic decomposition. An arrangement of these electrolytic reaction tanks may be in series, in parallel or a combination thereof, although an arrangement in series is convenient for completely treating organic compounds by electrolytic decomposition, while a combined arrangement is suitable for treating a large quantity of waste water all at once and completely decomposes organic compounds by electrolysis.

For example, in one embodiment, three electrolytic reaction tanks 1, 2 and 3 arranged in series, which are lined up in three rows A, B and C as shown in Fig. 2. Waste water in a waste water storage tank 4 is pumped to each of the first step electrolytic reaction tanks 1, 1 and 1 in each row A, B and C and to those tanks 2, 2 and 2 as well as 3, 3 and 3, in order, to subject a treatment by electrolytic decomposition, respectively and collected in a treated water tank 5.

It is important in this embodiment that the above mentioned requirement with regard to the current density and the liquid flow linear velocity is satisfied in each of electrolytic reaction tanks 1, 1 and 1.

Separation of gas contents may be conducted in combination with electrolytic decomposition in plural electrolytic reaction tanks to treat organic compounds-containing waste water by electrolytic decomposition.

In the above mentioned treatment, exit water from at least one of electrolytic reaction tanks or each thereof except those tanks of final step may be subjected to vapor-liquid separation by means of a vapor-liquid separator as described above or a liquid receiving tank provided with an upper vapor phase section and a vent section on a top portion thereof, and then pumped to and treated in subsequent electrolytic reaction tanks, or subjected to vapor-liquid separation in the electrolytic reaction tanks

themselves provided with an upper vapor phase section and a vent section on a top portion thereof similarly as described above, although at least one of these electrolytic reaction tanks or each thereof except those tanks of final step are excluded.

For example, two electrolytic tanks 1 and 2 are arranged in series, while a liquid receiving tank 6 provided with an upper vapor phase section and a vent section 6' on a top portion thereof is arranged between these first and second step electrolytic reaction tanks 1 and 2 as shown in Fig. 3. Waste water in a waste water storage tank 4 is introduced into the first step electrolytic reaction tank 1 to conduct the first step treatment by electrolytic decomposition and then is introduced into the water receiving tank 6 to separate gas contents formed through the first step electrolytic reaction, which is vented outside from the vent section 6'.

The liquid phase portion separated from the gas contents is introduced into the second step electrolytic reaction tank 2, subjected to the second step treatment by electrolytic decomposition and then stored in a treated water storage tank 5.

It is also important in this embodiment that the above mentioned requirement with regard to the current density and the liquid flow linear velocity is satisfied in each of the first and second electrolytic reaction tanks 1 and 2.

In another embodiment, the first step electrolytic reaction tank 11 itself is provided with an upper vapor phase section and a vent section 11' on a top portion thereof as shown in Fig. 4. Waste water in a waste water storage tank 4 may be introduced into the first step electrolytic reaction tank 11 to conduct the first step treatment by electrolytic decomposition while separating and removing gas contents formed thereby, followed by the second step treatment by electrolytic decomposition, and then stored in a treated water tank 5.

The second method for treating organic compounds-containing waste water

There will be described the second method for treating organic compounds-containing waste water of this invention. A characteristic feature of the second treating method is that a diamond electrode is used at least as an anode and pH of the waste water is adjusted to alkaline. With regard to kinds and concentration of the organic compounds to be treated, there is no limitation similarly as in the case of the first treating method.

A pH value of the waste water to be treated is not limited especially in the second treating method if the water is alkaline, but preferably it is 8 to 14, and more preferably 9 to 13.

A hydroxyl radical forming effect is decreased at values less than pH 8 so that the effectiveness thereof to oxidatively decompose the organic compounds is not

improved, while such the effectiveness is saturated at pH 14.

Adjustment of pH may be done by adding alkali metal or alkaline metal to waste water, or supplying additional waste water of higher pH values thereto.

In general, alkali metal or alkaline earth metal may be added as a compound thereof such as hydroxide and carbonate of the metal as it is, or dissolved in water to add as an aqueous solution.

As an important point of the second treating method is to conduct the treatment by electrolytic decomposition in the electrolytic reaction tank under a pH condition as described above, the alkali or alkaline earth metal may be added to waste water at any upstream side from exits of electrolytic reaction tanks, for example, a position just before the electrolytic reaction tanks, a waste water storage tank if a system comprises such a facility, or an exit portion of electrolytic reaction tank when waste water is recycled for further treatment.

It is preferable to conduct the treatment by checking whether a pH value in electrolytic reaction tanks is within a range of the above mentioned condition or not, even where the metal is added.

A diamond electrode used for electrochemically treating waste water of the above mentioned pH values may be the same as what is used in the first treating method. The treatment by electrolytic decomposition may be conducted by the use of a diamond electrode as a cathode while periodically changing cathode and anode.

In this case, it is preferable to conduct a contact treatment at the current density of 0.001 to 10 A/cm² on the surface of the diamond electrode and the liquid flow linear velocity of 10 to 10,000 m/hr by flowing the organic compounds-containing waste water in the direction parallel to the diamond electrode so as to decompose organic compounds by electrolysis effectively.

In order to treat large quantity of waste water from plants, etc. by electrolytic decomposition on a practical scale to reduce organic compounds contained therein to a predetermined level at current density less than 0.001 A/cm², there are required diamond electrodes of large surface area to some extent, electrolytic reaction tanks having large quantity and enormous system and running costs, although the current efficiency of diamond electrode is satisfactory.

At current density over 10 A/cm², on the contrary, voltage between electrodes is increased and consumed as thermal energy, which is uneconomical and not preferable from a standpoint of durability of diamond electrode.

The reason why the liquid flow of waste water is 10 to 10,000 m/hr in linear velocity is that insufficient contact time between the waste water and the electrode

surface hardly promotes electrolytic decomposition of organic compounds thoroughly at flow velocity over 10,000 m/hr, while treating efficacy of the waste water is extremely lowered because of an insufficient electrolytic effect at flow velocity less than 10 m/hr.

Especially, for the same reason as described in the first treatment method, it is preferable that the current density is 0.5 to 10 A/cm² and the liquid flow linear velocity is 200 to 10,000 m/hr and that the formulas 1 and 2 are satisfied.

Although a liquid temperature in the electrolytic reaction tanks is not limited especially, it is desirably about 10 to 95°C in the second treating method, because electrolytic decomposition of organic compounds proceeds insufficiently at excessively low temperatures, while considerable formation of gas contents inhibits contact between the waste water and the electrode surface.

In the second treating method of this invention, it is possible to treat organic compounds contained in waste water by electrolytic decomposition quite effectively using diamond electrodes while adjusting pH of the waste water to alkaline, which reduce the contact surface area due to satisfactory current density thereof, make the system scale small cause no trouble of acidic or basic corrosion due to remarkable chemical stability

Accordingly, waste water from plants, etc. can be electrochemically treated by means of a compact system on a practical scale so that organic compounds contained in the waste water are very easily decomposed to harmless inorganic compounds such as carbon dioxide and water without forming harmful and bad smelling byproducts.

The third method for treating organic compounds-containing waste water

There will be described the third method and system of this invention for treating organic compounds-containing waste water. A characteristic feature of the third treating method is that organic compounds-containing waste water to be treated contains organic suspended solids, while a decomposition mechanism thereof is the same as that of described in the first treating method. A system of this invention for treating organic compounds-containing waste water, which further contains organic suspended solids, is provided with diamond electrodes for treating such solids by electrolytic decomposition as an anode, or as both of an anode and a cathode to conduct change of electrodes.

In this system and method for treating organic compounds-containing waste water, it is not necessary to remove organic suspended solids contained in the waste water by a pretreatment such as filtration and coagulation-sedimentation so that the waste water can be directly supplied to the treating system, thereby the organic suspended solids and soluble organic substances contained in the waste water being

electrochemically oxidized and decomposed at the same time by means of diamond electrodes and finally removed.

A diamond electrodes used in the third treating method and system may be the same as that of used in the first treating method.

The diamond electrode has an extremely wider potential window compared with conventional metal electrodes such as platinum, which controls hydrogen and oxygen formed by electrolytic decomposition of water and, on the other hand, promotes formation of oxidizing agents such as ozone and hydroxyl radical, thereby only harmful organic substances to be oxidized and decomposed being effectively treated by oxidative decomposition. That is to say, when waste water which contains organic suspended solids is treated by electrolytic decomposition, the organic suspended solids are decomposed to soluble organic substances, followed by additional treatment by electrolytic decomposition to further decompose them and then removed. The organic suspended solids contained in waste water have been removed conventionally by a pretreatment and disposed as sludge, while they are decomposed and removed together with soluble organic substances therein at the same time without any pretreatment in this method.

In this case, it is preferable to conduct a contact treatment at the current density of 0.001 to 10 A/cm² on the surface of the diamond electrode and the liquid flow linear velocity of 10 to 10,000 m/hr by flowing the waste water which contains organic suspended solids in the direction parallel to the diamond electrode so as to decompose organic compounds by electrolysis effectively. The range of the current density and the liquid flow linear velocity to be used in this method is based on the same reason as described in the second treating method.

Especially, for the same reason as described in the first treatment method, it is preferable that the current density is 0.5 to 10 A/cm² and the liquid flow linear velocity is 200 to 10,000 m/hr and that the formulas 1 and 2 are satisfied.

Although a liquid temperature in the electrolytic reaction tanks is not limited especially, it is desirably about 10 to 95°C in the third treating method, because electrolytic decomposition of organic compounds promotes insufficiently at excessively low temperatures, while considerable formation of gas contents inhibits contact between the waste water and the electrode surface.

In the third treating method of this invention, it is possible to very effectively reduce total organic carbon (TOC) concentration and chemical oxygen demand (COD) of waste water which contains organic suspended solids, improve the electrolytic efficiency compared with a treatment by electrolytic decomposition using conventional

platinum type electrodes, decrease an electrode surface area to be required and minimize the electrolytic reaction system as a whole, which brings great economical merits. Especially, it is possible to keep removal of organic suspended solids and soluble organic substances at high efficiency by conducting change of electrodes using diamond electrodes as both of an anode and a cathode.

The fourth method for treating organic compounds-containing waste water

There will be described the fourth method of this invention for treating organic compounds-containing. A characteristic feature of the fourth treating method is that organic compounds-containing waste water to be treated contains organic nitrogen compounds and that the first step treatment by electrolytic decomposition is conducted using diamond electrodes as both of a cathode and an anode and then the second step treatment by electrolytic decomposition is conducted using the diamond electrode as a cathode and a metal electrode as an anode.

In this case, sulfate ions may be added to the waste water which contains organic nitrogen compounds when the first treatment by electrolytic decomposition is conducted and similarly, at the same time, chloride ions may be added to the waste water treated by the first step treatment when the second treatment by electrolytic decomposition is conducted.

Organic nitrogen compounds to be treated by the fourth treating method are not limited to specific ones if those compounds have nitrogen and may include any compound which can be decomposed by an electrolytic treatment to an inorganic compound such as carbon dioxide, nitrogen and water. Further, concentration of the organic nitrogen compounds is not limited specifically but may be any level, while the nitrogen compounds may be concentrated before the treatment, if necessary. It is preferable, however, that concentration of the organic nitrogen compounds is about 0.5 to 20 g/liter ("liter" and "milliliter" will hereinafter be referred to as "L" and "mL", respectively) from a standpoint of the electrolytic efficiency of the second step treatment in this treating method.

In the fourth treating method, total organic carbon(TOC) is primarily reduced in the first step and total organic nitrogen (T-N) is mainly lowered in the second step.

The first step treatment by electrolytic decomposition is conducted using diamond electrodes as both of a cathode and an anode.

When the diamond electrodes are used as both of cathode and an anode as described above, organic nitrogen compounds are oxidized to NO_x and nitrate ions on the anode and reduced to ammonia on the cathode, which is then oxidized to nitrate ions on the anode. Although oxidation and reduction are thus repeated between both

electrodes, ammonia formed on the cathode is subjected to the second step treatment by electrolytic decomposition before it is oxidized again on the anode, thereby re-oxidation thereof being prevented in this treating method.

If electrolytes which contain sulfate ion (SO_4^{2-}) is present in the system, formation of persulfuric acid ($\text{S}_2\text{O}_8^{2-}$) and ozone proceeds on the anode side of diamond electrodes, which synergistically contributes to the effect of strong oxidative decomposition.

These electrolytes which contain sulfate ion may include sulfates of alkali metal and alkaline earth metal such as potassium sulfate, sodium sulfate and calcium sulfate, or other compounds capable of forming sulfate ions. These electrolytes may either be used independently or any combination of two or more.

The electrolytes which contain sulfate ion may be present in organic nitrogen compounds-containing waste water to be treated by the fourth treatment method or introduced from outside.

Concentration of sulfate ion during the first step treatment by electrolytic decomposition is not limited to a specific level, but preferably is about 1 to 100 g/L in the fourth treating method. The above mentioned effect of sulfate ion is not exhibited at excessively lower concentration thereof, while such effect is saturated at excessively higher concentration and, in addition, the electrolytes themselves should be treated, which decreases the treatment efficiency.

It is preferable to conduct the first step treatment by electrolytic decomposition at current density of 0.1 to 10 A/cm² and liquid flow linear velocity of 200 to 10,000 m/hr. When the current density is less than 0.1 A/cm², electrodes of wider surface area and electrolytic reaction tanks of large quantity are required to treat a large amount of waste water which contains organic nitrogen compounds by electrolytic decomposition to reduce the compounds to a predetermined level, and when it is more than 10 A/cm², voltage between electrodes increases and is consumed as thermal energy, which is not preferable from a standpoint of durability of diamond electrodes.

The liquid flow linear velocity is preferably increased with an increase in the current density. In order to raise a TOC removal rate to 70 % or more in 3 hours within the above mentioned range of current density and to remove gas contents formed by the electrolytic reaction together with the liquid flow, it is important to increase the liquid flow linear velocity over 200 m/hr and is preferable to keep it in the range up to 10,000 m/hr.

Especially, for the same reason as described in the first treatment method, it is

preferable that the current density is 0.5 to 10 A/cm² and the liquid flow linear velocity is 200 to 10,000 m/hr and that the formulas 1 and 2 are satisfied.

Although a liquid temperature of the first step treatment by electrolytic decomposition is not limited especially, it is desirably about 10 to 95°C in the fourth treating method, because electrolytic decomposition of organic nitrogen compounds proceeds insufficiently at excessively low temperatures, while considerable formation of gas contents inhibits contact between the waste water and the electrode surface.

The waste water in which TOC is primarily reduced by the first treatment by electrolytic decomposition is subjected to the second treatment by electrolytic decomposition.

The second treatment by electrolytic decomposition is conducted using a diamond electrode as a cathode and a metal electrode as an anode.

There may be used an electrode made of platinum, palladium, rhodium, gold, silver and iridium as well as alloys thereof as the metal electrode.

There may also be used electrodes made of these metals or alloys of IrO₂-dispersed or supported types.

In the second step treatment by electrolytic decomposition, the waste water, in which TOC has been reduced by the first step treatment, is treated by electrolytic decomposition using the metal electrode as an anode and the diamond electrode as a cathode to reduce T-N

When chloride ions (Cl⁻, ClO⁻, etc.) are present in the waste water, quite effective reduction of T-N is achieved. The reason why is that hypochlorite ion is formed on the anode and reacts with ammonia formed by reduction of nitrate ion on the diamond cathode to form a nitrogen gas, which is released out of the system.

If the diamond electrode is used as an anode, however, oxidation ability thereof is excessively strong so that the chloride ion is oxidized to perchloric acid and the reaction as described above does not occur.

There may be used potassium chloride, sodium chloride, potassium hypochlorite, sodium hypochlorite, etc. as the electrolytes which contain the chloride ions and they may be used independently or any combination of two or more.

The electrolytes which contain chloride ions may be present in the organic nitrogen compounds-containing waste water to be treated by this treating method or be introduced from outside.

Concentration of chloride ions during the second step treatment by electrolytic decomposition of the fourth treating method is preferably about 500 to 12,000 mg/L, although it is not limited to a specific level.

As chloride ions are used for the purpose of raising the current efficiency as described above, concentration thereof is not necessarily so high in this treating method because a diamond electrode of high current efficiency is used as the cathode, and accordingly it is possible to get sufficient current efficiency under the concentration of 12,000 mg/L, around which the efficiency decreases in conventional treatment by electrolytic decomposition using platinum electrodes as both of a cathode and an anode. On the other hand, when the concentration is less than 500 mg/L, it is sometimes hard to obtain sufficient current efficiency to reduce T-N in the waste water through the treatment by electrolytic decomposition.

It is preferable to conduct the second step treatment by electrolytic decomposition at current density of 0.1 to 10 A/cm² and liquid flow linear velocity of 200 to 10,000 m/hr.

When the current density is less than 0.1 A/cm², electrodes of wider surface area and electrolytic reaction tanks of large quantity are required to reduce T-N in the waste water through the treatment by electrolytic decomposition to a predetermined level, and when it is more than 10 A/cm², voltage between electrodes increases and is consumed as thermal energy, which is not preferable from a standpoint of durability of diamond electrodes.

The liquid flow linear velocity is preferably increased with an increase in the current density. In order to raise a T-N removal rate to 70 % or more in 3 hours within the above mentioned range of current density and to remove gas contents formed by the electrolytic reaction together with the liquid flow, it is important to increase the liquid flow linear velocity over 200 m/hr and is preferable to keep it in the range up to 10,000 m/hr.

Especially, for the same reason as described in the first treatment method, it is preferable that the current density is 0.5 to 10 A/cm² and the liquid flow linear velocity is 200 to 10,000 m/hr and that the formulas 1 and 2 are satisfied.

Although a liquid temperature of the second step treatment by electrolytic decomposition is not limited especially, it is desirably about 10 to 95°C as similarly as the first step treatment by electrolytic decomposition, the reaction to reduce T-N proceeds insufficiently at excessively low temperatures, while considerable formation of gas contents inhibits contact between the waste water and the electrode surface.

There may be used the same diamond electrodes employed in the first treating method as those electrodes employed in the first and second step treatments by electrolytic decomposition.

In the fourth treating method, the first and second step treatments by

electrolytic decomposition may be continuously conducted in a serial arrangement of a first step electrolytic reaction tank 1 and a second step electrolytic reaction tank 2 as shown in Fig. 5, or in a batch-wise manner as shown in Fig. 6 in which a storage tank 3 is arranged between the first step electrolytic reaction tank 1 and the second step electrolytic reaction tank 2 so that waste water is once stored in the tank 3 after the first step treatment by electrolytic decomposition and then subjected to the second step treatment by electrolytic decomposition.

In Figs. 5 and 6, numeral 4 designates a storage tank for waste water to be treated and numeral 5 designates a storage tank for water after the second step treatment by electrolytic decomposition.

Further, according to this treating method, there may be used a plurality of each of the first and second step electrolytic reaction tanks 1 and 2 shown in Figs. 5 and 6, while an arrangement of each electrolytic reaction tank may be in series, in parallel or a combination thereof. A serial arrangement is suited for successfully treating organic nitrogen compounds-containing waste water by electrolytic decomposition, while a combination of parallel serial arrangements is appropriate for treating a large quantity of waste water at once and, at the same time, for successfully treating the organic nitrogen compounds-containing waste water by electrolytic decomposition.

As shown in Fig. 7, for example, three electrolytic reaction tanks 11, 12 and 13 for conducting the first step treatment by electrolytic decomposition are arranged in series, while three of serially arranged these tanks are further arranged in three parallel rows A, B and C. Waste water is supplied from the waste water storage tank 4 to the first electrolytic reaction tanks 11, 11 and 11 of each row A, B and C, and to the second and then the third electrolytic reaction tanks 12, 12 and 12 as well as 13, 13 and 13 one after another to conduct the first step treatment by electrolytic decomposition, and is collected in the storage tank 3.

With regard to the second step treatment by electrolytic decomposition, electrolytic reaction tanks are arranged in series (21, 22 and 23) and in parallel (rows A, B and C) in a similar manner as described above. The water is supplied from the storage tank 3 to the first electrolytic reaction tanks 21, 21 and 21 of each of rows A, B and C, and then the second and the third electrolytic reaction tanks 22, 22 and 22 as well as 23, 23 and 23 one after another to conduct the second step treatment by electrolytic decomposition, which is collected in the storage tank 5.

It is desirable in this embodiment that each of electrolytic reaction tanks 11, 12 and 13 satisfies the above mentioned requirements of the first step treatment by

electrolytic decomposition and also each of electrolytic reaction tanks 21, 22 and 23 satisfies the above mentioned requirements of the first step treatment by electrolytic decomposition.

In the fourth treating method, waste water which contains organic compounds, such as those contained in plant waste water, is subjected to the first step treatment by electrolytic decomposition using diamond electrodes as both of a cathode and an anode, thereby TOC being very effectively decreased. The diamond electrode makes it possible to reduce the contact surface area due to satisfactory current efficiency thereof and to minimize the system, and has no concern for acid or alkali corrosion due to its outstanding chemical stability.

The waste water, in which corrosive TOC has thus been decreased, is subjected to the second step treatment by electrolytic decomposition using metal electrodes as an anode and diamond electrodes as a cathode only, thereby T·N being decreased effectively.

As a result, waste water from plans, etc. can be quite easily decomposed by an electrochemical treatment of organic nitrogen compounds contained therein to form harmless inorganic compounds such as carbon dioxide, nitrogen gas and water in a compact system on a practical scale while keeping a system cost low.

Examples

The first treating method

Example 1

Two of laminated polycrystal diamond electrode plates (5 x 5 x 0.05 cm) synthesized by vapor phase deposition using a boron doping method were used as both of a cathode and an anode keeping a space of 1 cm between them to constitute an electrolytic reaction tank.

On the other hand, 1.5 L of waste water (TOC: 710 mg/L) which contains dimethyl sulfoxide (DMSO) as an organic compound was prepared, followed by addition of 14,200 mg/L of sodium sulfate thereto, and stored in a storage tank.

Making quantity of electricity to the diamond electrodes was controlled to yield current density of 1 A/cm², while the waste water in the storage tank was introduced to the electrolytic reaction tank by adjusting a pumping rate at 1,500 m/hr of liquid flow linear velocity, taken out of the electrolytic tank as exit water and returned to the storage tank for a circulating treatment.

The waste water in the storage tank was agitated by means of a stirrer.

After the circulating treatment was conducted continuously for three hours,

water from an exit of the electrolytic reaction tank was collected for total organic carbon (TOC) analysis.

It was confirmed that TOC is effectively decomposed and removed from the result shown in Table 1.

Table 1

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	710
1	230
2	50
3	6

Comparative Example 1

The circulating treatment was conducted continuously for three hours in a similar manner as described in Example 1 except changing the liquid flow linear velocity to 100 m/hr.

The result is shown in Table 2. It was confirmed that a rate of TOC decomposition and removal remains at about 50 % and further observed marks where a diamond thin layer comes off after the treatment by electrolytic decomposition.

Table 2

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	710
1	620
2	450
3	346

Example 2

The circulating treatment was conducted continuously for three hours in a similar manner as described in Example 1 using 3L of waste water (TOC: 770 mg/L) which contains tetramethyl ammonium hydrazide as an organic compound at the current density of 2 A/cm² and the liquid flow linear velocity of 2,600 m/hr.

The result is shown in Table 3. It was confirmed that TOC is effectively decomposed and removed similarly as in Example 1.

Table 3

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	770
1	215

2	42
3	6

Comparative Example 2

The circulating treatment was conducted continuously for three hours in a similar manner as described in Example 2 except changing the liquid flow linear velocity to 500 m/hr.

The result is shown in Table 4. It was confirmed that a rate of TOC decomposition and removal remains at about 50 % and further observed marks where a diamond thin layer comes off after the treatment by electrolytic decomposition.

Table 4

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	770
1	550
2	467
3	388

The second treating method

Example 3

Two of laminated polycrystal diamond electrode plates (5 x 5 x 0.05 cm) synthesized by vapor phase deposition using a boron doping method were used as both of a cathode and an anode keeping a space of 1 cm between them to constitute an electrolytic reaction tank.

On the other hand, 300 mL of waste water (DMSO: 2,300 mg/L; TOC: 710 mg/L) which contains dimethyl sulfoxide (DMSO) as an organic compound was prepared, followed by addition of 4,000 mg/L of sodium hydroxide thereto to adjust the pH value to 12, and stored in a storage tank.

Making quantity of electricity to the diamond electrodes was controlled to yield current density of 0.2 A/cm² (2,000 A/cm²) while the waste water in the storage tank was introduced to the electrolytic reaction tank by adjusting a pumping rate at 100 m/hr (flow rate 833 mL/min) of liquid flow linear velocity, taken out of the electrolytic tank as exit water and returned to the storage tank for a circulating treatment.

The waste water in the storage tank was agitated by means of a stirrer.

After the circulating treatment was conducted continuously for three hours, water from an exit of the electrolytic reaction tank was collected for total organic

carbon (TOC) analysis.

It was confirmed that TOC is effectively decomposed and removed from the result shown in Table 5.

Table 5

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	710
1	170
2	20
3	5

Comparative Example 3

The circulating treatment was conducted continuously for three hours in a similar manner as described in Example 3 except adding 6,000 mg/L of sodium chloride instead of sodium hydroxide without adjusting the pH value (pH 6.8).

The result is shown in Table 6. It was confirmed that an effect of TOC decomposition and removal is markedly decreased.

Table 6

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	710
1	680
2	650
3	620

Example 4

The circulating treatment was conducted continuously for three hours in a similar manner as described in Example 3 except using 600 mL of waste water (dioxane: 600 mg/L; TOC: 313 mg/L) which contains dioxane as an organic compound.

It was confirmed that TOC is effectively decomposed and removed from the result shown in Table 7.

Table 7

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	313
1	165
2	42
3	6

Comparative Example 4

The circulating treatment was conducted continuously for three hours in a similar manner as described in Example 4 except adding 6,000 mg/L of sodium chloride instead of sodium hydroxide without adjusting the pH value (pH 6.7).

The result is shown in Table 2. It was confirmed that an effect of TOC decomposition and removal is markedly decreased.

Table 8

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	313
1	285
2	270
3	260

Example 5

Two of smaller diamond electrodes (2 x 2.5 x 0.05 cm) than those electrodes used in Example 3 were used as both of a cathode and an anode keeping a space of 1 cm between them to constitute an electrolytic reaction tank.

The circulating treatment was conducted continuously for three hours in a similar manner as described in Example 3 except that the current density is 1 A/cm² (10,000 A/m²) and the liquid flow linear velocity is 1,000 m/hr (flow rate: 3,300 mL/min).

The result is shown in Table 9. It was confirmed that an effect of TOC decomposition and removal is better than the result of Example 3 and the electrolytic reaction tank is capable of being compact.

Table 9

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	710
1	145
2	12
3	< 1

Example 6

The circulating treatment was conducted continuously for three hours in a similar manner as described in Example 4 except that constitution of an electrolytic reaction tank and current density as well as liquid flow linear velocity are the same as those of Example 5.

The result is shown in Table 10. It was confirmed that an effect of TOC decomposition and removal is better than the result of Example 3 and the electrolytic reaction tank is capable of being compact.

Table 10

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>
0	313
1	143
2	35
3	< 1

The third treating method

Example 7

Two of laminated polycrystal diamond electrode plates (5 cm x 5 cm x 0.05 cm) synthesized by vapor phase deposition using a boron doping method were used as both of a cathode and an anode keeping a space of 1 cm between them to constitute an electrolytic reaction tank.

A portion of 500 mL of waste water (SS = 720 mg/L; TOC = 1894 mg/L; COD_{Cr} = 8,240 mg/L) which contains organic suspended solids (SS) and added with 14,000 mg/L of sodium sulfide as an electrolyte) was charged in a storage tank and pumped to the electrolytic reaction tank in an agitated condition by means of a stirrer at a flow rate of 500 mL/min (liquid flow linear velocity 60 m/hr) for a circulating treatment. Making quantity of electricity was controlled to yield current density of 0.1 A/cm² (1,000 A/m²). The treatment by electrolytic decomposition was continued for 6 hours and collected water at an exit of the electrolytic reaction tank for analysis of TOC, SS, COD_{Cr} and turbidity. The result obtained is shown in Fig. 11. It is confirmed that organic suspended solids can be effectively removed together with TOC and COD_{Cr}.

Table 11

Time of electrolytic decomposition (hr)	SS (mg/L)	TOC (mg/L)	COD _{Cr} (mg/L)	Turbidity (degree)
0	720	1,894	8,240	705
2	< 5	829	2,720	< 1
4	< 5	218	540	< 1
6	< 5	16	30	< 1

Comparative Example 5

A treatment by electrolytic decomposition was conducted under the same condition of Example 7 except that two of platinum plated titanium plates (5 cm x 5 cm x 0.3 cm) as electrodes instead of electrically conductive diamond plates used in Example 7. The electrolytic decomposition was continued for 6 hours similarly as in the case of Example 7, but deposition of SS on the electrodes was occurred and, in addition, there was no effect to decrease TOC and CODcr as shown in analysis of Table 12.

Table 12

Time of electrolytic decomposition (hr)	SS (mg/L)	TOC (mg/L)	CODcr (mg/L)	Turbidity (degree)
0	720	1,894	8,240	705
2	88	1,605	6,200	55
4	32	1,445	5,020	34
6	21	1,303	4,820	32

Example 8

Two of laminated polycrystal diamond electrode plates (5 cm x 5 cm x 0.05 cm) synthesized by vapor phase deposition using a boron doping method were used as both of a cathode and an anode keeping a space of 5 mm between them to constitute an electrolytic reaction tank.

A portion of 500 mL of waste water (SS = 720 mg/L; TOC = 1894 mg/L; CODcr = 8,240 mg/L) which contains organic suspended solids (SS) and added with 14,000 mg/L of sodium sulfide as an electrolyte) was charged in a storage tank and pumped to the electrolytic reaction tank in an agitated condition by means of a stirrer at a flow rate of 3 L/min (liquid flow linear velocity 720 m/hr) for a circulating treatment. Making quantity of electricity was controlled to yield current density of 0.1 A/cm² (1,000 A/m²).

The treatment by electrolytic decomposition was continued for 5 hours and collected water at an exit of the electrolytic reaction tank for analysis of TOC, SS, CODcr and turbidity. The result obtained is shown in Fig. 13. It is confirmed that the treatment can be completed in a shorter time than that of Example 7 by increasing the liquid flow linear velocity compared with Example 7.

Table 13

Time of electrolytic decomposition (hr)	SS (mg/L)	TOC (mg/L)	CODcr (mg/L)	Turbidity (degree)
0	720	1,894	8,240	705

1	< 5	1,175	3,890	< 1
2	< 5	729	1,650	< 1
3	< 5	456	540	< 1
4	< 5	168	350	< 1
5	< 5	5	20	< 1

Example 9

Two of laminated polycrystal diamond electrode plates of disk type (10 cm in diameter x 0.05 cm) synthesized by vapor phase deposition using a boron doping method were used as both of a cathode and an anode keeping a space of 5 mm between them to constitute an electrolytic reaction tank.

A portion of 6 L of waste water (SS = 120 mg/L; TOC = 950 mg/L; COD_{Cr} = 3,240 mg/L) which contains organic suspended solids (SS) and added with 14,000 mg/L of sodium sulfide as an electrolyte) was charged in a storage tank and pumped to the electrolytic reaction tank in an agitated condition by means of a stirrer at a flow rate of 5 L/min (liquid flow linear velocity 600 m/hr) for a circulating treatment. Making quantity of electricity was controlled to yield current density of 0.5 A/cm² (5,000 A/m²). The treatment by electrolytic decomposition was continued for 5 hours and collected water at an exit of the electrolytic reaction tank for analysis of TOC, SS, COD_{Cr} and turbidity. The result obtained is shown in Fig. 14.

Table 14

Time of electrolytic decomposition (hr)	SS (mg/L)	TOC (mg/L)	COD _{Cr} (mg/L)	Turbidity (degree)
0	120	950	3,240	650
2	25	329	1,650	105
4	< 5	124	550	24
6	< 5	32	96	< 1

Comparative Example 6

A treatment by electrolytic decomposition was conducted under the same condition of Example 9 except that two of platinum plated titanium plates of disk type (10 cm in diameter x 0.3 cm) as electrodes instead of electrically conductive diamond plates used in Example 7. The electrolytic decomposition was continued for 6 hours similarly as in the case of Example 9, but deposition of SS on the electrodes was occurred and, in addition, there was no effect to decrease TOC and COD_{Cr} as shown in analysis of Table 15.

Table 15

Time of				
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electrolytic decomposition (hr)	SS (mg/L)	TOC (mg/L)	CODcr (mg/L)	Turbidity (degree)
0	120	950	3,240	650
2	68	695	2,200	350
4	55	586	2,020	340
6	48	534	1,850	320

Example 10

Two of laminated polycrystal diamond electrode plates of disk type (10 cm in diameter x 0.05 cm) synthesized by vapor phase deposition using a boron doping method were used as both of a cathode and an anode keeping a space of 5 mm between them to constitute an electrolytic reaction tank.

A portion of 6 L of waste water (SS = 120 mg/L; TOC = 950 mg/L; CODcr = 3,240 mg/L) which contains organic suspended solids (SS) and added with 14,000 mg/L of sodium sulfide as an electrolyte) was charged in a storage tank and pumped to the electrolytic reaction tank in an agitated condition by means of a stirrer at a flow rate of 10 L/min (liquid flow linear velocity 1,200 m/hr) for a circulating treatment. Making quantity of electricity was controlled to yield current density of 0.5 A/cm² (5,000 A/m²). The treatment by electrolytic decomposition was continued for 5 hours and collected water at an exit of the electrolytic reaction tank for analysis of TOC, SS, CODcr and turbidity. The result obtained is shown in Fig. 16. It is clear that an effect of treatment by electrolytic decomposition is improved compared with that of Example 9 by increasing the liquid flow linear velocity.

Table 16

Time of electrolytic decomposition (hr)	SS (mg/L)	TOC (mg/L)	CODcr (mg/L)	Turbidity (degree)
0	120	950	3,240	650
2	< 5	270	1,350	< 1
4	< 5	88	320	< 1
6	< 5	8	25	< 1

The fourth treating method

Example 11

Two of laminated polycrystal diamond electrode plates (5 x 5 x 0.05 cm) synthesized by vapor phase deposition using a boron doping method were used as both of a cathode and an anode keeping a space of 1 cm between them to constitute an electrolytic reaction tank for conducting the first step treatment by electrolytic

decomposition.

On the other hand, 300 mL of waste water (TOC: 770 mg/L and T-N: 230 mg/L) which contains tetramethyl ammonium hydroxide as an organic nitrogen compound was prepared, followed by addition of 14,200 mg/L of sodium sulfate thereto, and stored in a storage tank.

Making quantity of electricity to the diamond electrodes was controlled to yield current density of 0.2 A/cm² (2,000 A/cm²) while the waste water in the storage tank was introduced to the electrolytic reaction tank by adjusting a pumping rate at 200 m/hr of liquid flow linear velocity with agitation of the water in the storage tank by means of a stirrer, while overflowed water from the electrolytic reaction tank was returned to the storage tank for a circulating treatment.

After the circulating treatment was conducted continuously for three hours, water from an exit of the electrolytic reaction tank was collected for analyzing total organic carbon (TOC) and total organic nitrogen (T-N).

It was confirmed that TOC is effectively decomposed and removed from the result shown in Table 17.

Table 17

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>	<u>T-N(mg/L)</u>
0	770	230
1	230	190
2	50	165
3	6	140

Then, the same diamond electrode as that of used in the first step electrolytic reaction tank was used as a cathode and a platinum-plated titanium electrode of plate type (5 x 5 x 0.3 cm) (hereinafter referred to as titanium-platinum electrode) was used as an anode to constitute an electrolytic reaction tank for the second step treatment by electrolytic decomposition. Using this electrolytic reaction tank, the waste water which has been continuously treated by the first electrolytic decomposition for three hours was subjected to the second step treatment by electrolytic decomposition as in the following.

The circulating treatment was continuously conducted for one hour in a similar manner as the first step treatment by electrolytic decomposition except that 6,000 mg/L of sodium chloride was added to the waste water treated by the first step electrolytic decomposition and the making quantity of electricity to both of a cathode and an anode is controlled to yield current density of 0.2 A/cm² (2,000 A/cm²).

The water was collected from a exit of the electrolytic reaction tank for

analysis of total organic nitrogen (T-N). The result is shown in Table 18. It was confirmed that T-N, which was not decomposed and removed sufficiently by the first step treatment by electrolytic decomposition, can be decomposed and removed effectively.

Table 18

<u>Time of electrolytic decomposition (hr)</u>	<u>T-N (mg/L)</u>
0	140
1	6

Comparative Example 7

The circulating treatment was conducted in a similar manner as Example 11 except that only the first step treatment by electrolytic decomposition was continuously conducted for 4 /hours.

The result is shown in Table 19. TOC was decomposed and removed similarly as Example 11, but the T-N removal rate was about 40 %.

Table 19

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>	<u>T-N(mg/L)</u>
0	770	230
1	234	196
2	52	160
3	8	136
4	< 1	125

Example 12

The circulating treatment was continuously conducted for three hours in a similar manner as the first step treatment by electrolytic decomposition of Example 11 except using 300 mL of waste water (TOC: 526 mg/L and T-N: 246 mg/L) which contains dimethylimidazolidinone as an organic compound.

The result is shown in Table 20. It was confirmed that TOC is effectively decomposed and removed similarly as the first step treatment by electrolytic decomposition of Example 11.

Table 20

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>	<u>T-N(mg/L)</u>
0	526	246
1	317	185
2	60	165

3

6

135

Then, the waste water was subjected to the second step treatment by electrolytic decomposition in a similar manner as that of Example 11 and collected the water at an exit of the electrolytic reaction tank for analysis of total organic nitrogen (T-N).

The result is shown in Table 21. It was confirmed that T-N, which was not decomposed and removed sufficiently by the first step treatment by electrolytic decomposition, can be decomposed and removed effectively.

Table 21

<u>Time of electrolytic decomposition (hr)</u>	<u>T-N (mg/L)</u>
0	135
1	6

Comparative Example 8

The circulating treatment was conducted in a similar manner as Example 12 except that only the first step treatment by electrolytic decomposition was continuously conducted for 4 hours.

The result is shown in Table 22. TOC was decomposed and removed similarly as Example 12, but the T-N removal rate was about 40 %.

Table 22

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>	<u>T-N(mg/L)</u>
0	526	246
1	308	196
2	52	160
3	5	136
4	< 1	115

Example 13

Two of laminated polycrystal diamond electrode plates (10 cm in diameter x 0.05 cm) synthesized by vapor phase deposition using a boron doping method were used as both of a cathode and an anode keeping a space of 1 cm between them to constitute an electrolytic reaction tank for conducting the first step treatment by electrolytic decomposition.

On the other hand, 4 L of waste water (TOC: 1,000 mg/L and T-N: 290 mg/L) which contains tetramethyl ammonium hydroxide as an organic nitrogen compound was prepared, followed by addition of 14,200 mg/L of sodium sulfate thereto, and stored

in a storage tank.

Making quantity of electricity to the diamond electrodes was controlled to yield current density of 0.5 A/cm^2 ($5,000 \text{ A/cm}^2$) while the waste water in the storage tank was introduced to the electrolytic reaction tank by adjusting a pumping rate at $2,000 \text{ m/hr}$ of liquid flow linear velocity with agitation of the water in the storage tank by means of a stirrer and conducted a circulating treatment. After the circulating treatment was conducted continuously for 6 hours, water from an exit of the electrolytic reaction tank was collected for analyzing total organic carbon (TOC) and total organic nitrogen (T-N). It was confirmed that TOC is effectively decomposed and removed from the result shown in Table 23.

Table 23

<u>Time of electrolytic decomposition (hr)</u>	<u>TOC (mg/L)</u>	<u>T-N(mg/L)</u>
0	1,000	290
1	475	263
2	284	224
3	134	193
4	39	162
5	5	131

Then, the same diamond electrode as that of used in the first step electrolytic reaction tank was used as a cathode and a platinum-plated titanium electrode of plate type (10 cm in diameter x 0.05 cm) was used as an anode to constitute an electrolytic reaction tank for the second step treatment by electrolytic decomposition. Further, using this electrolytic reaction tank, the waste water which has been continuously treated by the first electrolytic decomposition was subjected to the second step treatment by electrolytic decomposition as in the following.

The circulating treatment was continuously conducted for one hour in a similar manner as the first step treatment by electrolytic decomposition except that $6,000 \text{ mg/L}$ of sodium chloride was added to the waste water treated by the first step electrolytic decomposition and the making quantity of electricity is controlled to yield current density of 0.5 A/cm^2 ($5,000 \text{ A/cm}^2$).

The water was collected from an exit of the electrolytic reaction tank for analysis of total organic nitrogen (T-N). The result is shown in Table 24. It was confirmed that T-N, which was not decomposed and removed sufficiently by the first step treatment by electrolytic decomposition, can be decomposed and removed effectively.

Table 24

<u>Time of electrolytic decomposition (hr)</u>	<u>T-N (mg/L)</u>
0	131
1	52
2	4

Industrial Applicability

According to the first and second methods for treating organic compounds-containing waste water, organic compounds in waste water from plants, etc. can be easily decomposed to harmless inorganic compounds such as carbon dioxide and water without forming harmful and bad-smelling byproducts. The waste water from plants, etc. can also be treated by electrolytic decomposition economically on a practical scale using diamond electrodes of satisfactory current efficiency, thereby a system to be used being made compact, while durability of the diamond electrodes being extended because of chemical stability thereof.

Further, according to the third method for treating organic compounds-containing waste water and a system used thereby, it is possible to put down a treating cost of organic suspended solids and, at the same time, to control a great decrease in energy efficiency and a considerable reduction of system durability caused by electrolytic decomposition treatment of waste water which contains organic suspended solids. More precisely, soluble organic substances and organic suspended solids contained in waste water can be concurrently decomposed and removed to reduce total organic carbon (TOC) and chemical oxygen demand (COD) in the waste water by an oxidative decomposition treatment of them together without removing such solids in advance.

Furthermore, according to the fourth method for treating organic compounds-containing waste water, organic nitrogen compounds contained in waste water from plants, etc. can be easily decomposed to harmless inorganic compounds such as carbon dioxide, nitrogen gas and water. Waste water from plants, etc. can also be treated by a electrolytic decomposition treatment economically on a practical scale in which waste water which contains a large amount of organic nitrogen compounds is electrochemically treated by the first step electrolytic decomposition treatment using diamond electrodes of outstanding chemical stability and satisfactory current efficiency as both of a cathode and an anode and then electrochemically treated by the second step electrolytic decomposition treatment using the diamond electrode only as a cathode, thereby the system being made compact as a whole and cheap, while durability of electrodes being extended.

What is claimed is:

1. A method for electrochemically detoxifying organic compounds contained in waste water using diamond electrodes at least as an anode, in which current density is 0.5 to 10 A/cm² and liquid flow linear velocity is 200 to 10,000 m/hr.
2. A method for electrochemically detoxifying organic compounds contained in waste water, in which diamond electrodes are used at least as an anode, while pH of the waste water is adjusted to be alkaline.
3. A method for electrochemically detoxifying organic suspended solids contained in waste water as organic compounds, in which diamond electrodes are used at least as an anode to treat the organic suspended solids by electrolytic decomposition.
4. A method claimed in claim 1, 2 or 3 in which diamond electrodes are used as both of an anode and a cathode to undergo change of electrodes.
5. A method for electrochemically detoxifying organic nitrogen compounds contained in waste water as organic compounds, in which a first step treatment by electrolytic decomposition is conducted using diamond electrodes as an anode and a cathode, and then a second step treatment by electrolytic decomposition is conducted using the diamond electrodes as a cathode and metal electrodes as an anode.
6. A method claimed in claim 5 in which sulfate ions are added to organic compounds-containing waste water when a first step treatment by electrolytic decomposition is conducted.

7. A method claimed in claim 5 or 6 in which chloride ions are added to waste water after a first step treatment thereof by electrolytic decomposition when a second step treatment by electrolytic composition is conducted.
8. A method claimed in any one of claims 2 to 7 for treating waste water by electrolytic decomposition using diamond electrodes, in which current density on the surface of diamond electrodes is 0.001 to 10 A/cm² and liquid flow linear velocity is 10 to 10,000 m/hr during the treatment by electrolytic decomposition.
9. A method claimed in any one of claims 2 to 8 for treating waste water by electrolytic decomposition using diamond electrodes, in which current density on the surface of diamond electrodes is 0.5 to 10 A/cm² and liquid flow linear velocity is 200 to 10,000 m/hr during the treatment by electrolytic decomposition.
10. A method for controlling liquid flow linear velocity of the treatment by electrolytic decomposition in a method claimed any one of said claims 1 to 9 so as to satisfy the following formula 1:

$$\text{Formula 1: liquid flow linear velocity (m/hr)} \geq 400 \times (\text{current density (A/cm}^2\text{)} - 0.5) + 200$$

11. A method for controlling liquid flow linear velocity of the treatment by electrolytic decomposition in a method claimed any one of said claims 1 to 10 so as to satisfy the following formula 2:

$$\text{Formula 2: liquid flow linear velocity (m/hr)} \geq 1,000 \times (\text{current density (A/cm}^2\text{)} - 0.5) + 200$$

12. A system for treating organic compounds-containing waste water which comprises diamond electrodes to conduct a treatment by electrolytic decomposition of organic suspended solids contained in waste water as organic compounds.
13. A system for treating organic compounds-containing waste water claimed in claim 12 in which a treatment by electrolytic decomposition using diamond electrodes is conducted at current density of 0.001 to 10 A/cm² and liquid flow linear velocity of 10 to 10,000 m/hr.
14. A system for treating organic compounds-containing waste water claimed in claim 12 or 13 in which change of electrodes are conducted using diamond electrodes for both of a cathode and an anode.